

REMARKS**Summary of the Office Action**

The Office Action indicates that the Information Disclosure Statement filed on October 28, 2005 fails to comply with 37 C.F.R. § 1.98(a)(3) because it does not include a concise explanation of the relevance.

Claim 5 is objected to under 37 C.F.R. § 1.75(c) as being in improper form because it is a multiple dependent claim dependent on another multiple dependent claim.

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 5,176,760 to Young ("Young").

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Japanese Patent No. 03-006362 ("JP '362") or Japanese Patent No. 04-168273 ("JP '273").

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Japanese Patent No. 04-254577 ("JP '577").

Summary of the Response to the Office Action

Claims 1, 3, and 5-7 are presently pending. Claims 1, 4, and 5 have been amended. Claims 2 and 4 have been cancelled. New claims 6 and 7 have been added.

Information Disclosure Statement

The Office Action indicates that the Information Disclosure Statement filed on October 28, 2005 fails to comply with 37 C.F.R. § 1.98(a)(3) because it does not include a concise

explanation of the relevance. The relevance of the Takateru Umeda et al. reference can be found on the PCT Search Report submitted with the Information Disclosure Statement.

The Dearnley reference is also attached in the interest of completeness.

Objection under 35 U.S.C. § 175(c)

Claim 5 is objected to under 37 C.F.R. § 1.75(c) as being in improper form because it is a multiple dependent claim dependent on another multiple dependent claim. Claim 3 has been amended and claim 2 eliminated to obviate the objection.

Rejections under 35 U.S.C. § 103(a)

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Young. Applicants respectfully traverse the rejection.

Young does not teach or suggest that the content of carbon is 0.01% by weight or less.

In light of the above arguments, Applicants respectfully request that the rejection of claims 1-4 under 35 U.S.C. § 103(a) as being unpatentable over Young be withdrawn.

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over JP '362 or JP '273.

JP '362 and JP '273 do not teach or suggest that the content of carbon is 0.01% by weight or less. The SUS 304 stainless steel, etc., used in the examples has a higher carbon content than the claimed range. Applicants respectfully traverse the rejection.

In light of the above arguments, Applicants respectfully request that the rejection of claims 1-4 under 35 U.S.C. § 103(a) as being unpatentable over JP '362 or JP '273 be withdrawn.

Claims 1 to 4 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Japanese Patent No. 04-254577 ("JP '577). Applicants respectfully traverse the rejection.

Although JP '577 teaches that the content of carbon is 5% by weight or less the structure of the flange, the structure of the flange is such that a stainless steel alloy film or a stainless steel nitride film is formed on the sealing surface of an aluminum alloy flange part, and this structure is different from the structure recited in the present claims. Although the technology of JP '577 has a function of protecting the sealing surface of the flange from damage, it does not have a seal function and it is necessary to insert a sealing material such as a gasket between the flanges. This is because the inside of the flange of JP '577 is constituted of an aluminum alloy. Aluminum alloys and ultra-low carbon stainless steels are different in terms of their modulus of elasticity, and sealing surfaces having an aluminum alloy inside have a low sealing function in comparison with the ultra-low carbon stainless steel.

In addition, the Office Action asserts that "JP '577 teaches... ion plating [or sputtering] that closely meets the recited claims," although the claims call for "an ion implantation method" instead. The differences in ion plating, sputtering, and ion implantation are explained in the attached passages on ion implantation and sputtering from Van Nostrand's Scientific Encyclopedia (8th ed. 1995).

Furthermore, with regard to claim 5, none of the cited references teach or suggest dehydrogenated ultra-low carbon stainless steel. When dehydrogenated, the material can be used

under a high temperature – e.g., 400° C or higher. Although the Office Action states that the dehydrogenation in advance of the steel surface is not a patentable consideration and that “Applicant will have the burden to show that prior art product does not necessarily or inherently possess the characteristics of the claimed product,” none of the references disclose or suggest dehydrogenation at all. Thus, the stainless steels in the cited prior art would not possess the characteristics of the claimed product.

In light of the above arguments, Applicants respectfully request that the rejection of claims 1-4 under 35 U.S.C. § 103(a) as being unpatentable over JP ‘577 be withdrawn.

New Claims

New claims 6 and 7 have been added. Claim 6 recites that the ultra-low carbon stainless steel is dehydrogenated. As explained above, none of the cited references disclose dehydrogenated stainless steel. For at least that reason, Applicants respectfully assert that claims 6 and 7 are in condition for allowance.

Applicants believe that claims 1, 3, and 5-7 are in condition for allowance. Allowance of claims 1, 3, and 5-7 is requested.

CONCLUSION

In view of the foregoing, Applicants respectfully request reconsideration and the timely allowance of the pending claims. Should the Examiner feel that there are any issues outstanding after consideration of this response, the Examiner is invited to contact Applicants' undersigned representative to expedite prosecution.

If there are any other fees due in connection with the filing of this response, please charge the fees to our Deposit Account No. 50-0310. If a fee is required for an extension of time under 37 C.F.R. § 1.136 not accounted for above, such an extension is requested and the fee should also be charged to our Deposit Account.

Respectfully submitted,

MORGAN, LEWIS & BOCKIUS LLP

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By:



Kent Basson

Registration No. 48,125

CUSTOMER NO. 009629
MORGAN, LEWIS & BOCKIUS LLP
1111 Pennsylvania Avenue, N.W.
Washington, D.C. 20004
202.739.3000

XP 237 2828

Adhesive, Abrasive and Oxidative Wear in Ion-implanted Metals*

G. DEARNALEY

Nuclear Physics Division, Atomic Energy Research Establishment, Harwell, Oxon. OX11 0RA (Gt. Britain)

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ABSTRACT

Ion implantation is increasingly being used to provide wear resistance in metals and cemented tungsten carbides. Field trials and laboratory tests indicate that the best performance is achieved in mild abrasive wear. This can be understood in terms of the classification of wear modes (adhesive, abrasive, oxidative etc.) introduced by Burwell. Surface hardening and work hardenability are the major properties to be enhanced by ion implantation. The implantation of nitrogen or dual implants of metallic and interstitial species are effective. Recently developed techniques of ion-beam-enhanced deposition of coatings can further improve wear resistance by lessening adhesion and oxidation. In order to support such hard coatings, ion implantation of nitrogen can be used as a preliminary treatment.

There is thus emerging a versatile group of related hard vacuum treatments involving intense beams of nitrogen ions for the purpose of tailoring metal surfaces to resist wear.

1. INTRODUCTION

Ion implantation is increasingly being used as a means of providing wear resistance in metals, and particularly in alloy steels. A growing number of industrial centres are being established to carry out the process. There is also a possibility that implantation of varied species will enable some clarification by research studies of the complex mechanisms involved in wear. This has proved true in corrosion science, in which the versatility

of ion implantation is valued as a means of preparing coupons for test.

It is useful to divide wear mechanisms into a number of different categories. Burwell [1] distinguished three major processes, namely adhesive, abrasive and corrosive wear, together with four of lesser importance for the present discussion, namely particulate erosion, cavitation, fretting and surface fracture wear (by cracking in brittle materials). In a recent paper, Dearnaley [2] has argued that on the basis of observations and industrial tests made on nitrogen-implanted alloys it is possible to make useful distinctions between adhesive, abrasive and corrosive (including oxidative) wear, although some researchers [3] prefer to classify wear simply according to whether it is mild or severe.

The purpose of such analysis of wear modes has been to aid the optimization and efficient use of what is still a relatively expensive hard vacuum process. There is scope for the improvement not only in the cost-to-benefit ratio but also in the marketability of the process.

The present paper is designed to extend further this discussion of wear mechanisms in ion-implanted metals and in particular to explore the interaction between mechanical and more chemical, e.g. oxidative, processes during sliding wear. One objective of the paper will be to examine whether present ion implantation methods can be improved in order to force the wear process into a more favourable mode, i.e. from severe to mild. In this respect it is the ability of ion implantation, together with more recent developments such as ion beam mixing of deposited coatings, to tailor material composition and properties in the outer micron layer that is of value. Much of the technology for these treatments has been stimulated by the needs of the silicon device industry, and this remains a

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powerful driving force. Intense ion beams (of the order of 100 mA for gases) are now available, and this enables surface modifications to be made much more rapidly and in a wider range of materials applications.

3. WEAR MECHANISMS

Adhesive wear occurs when the pressure between sliding surfaces is high enough to cause local plastic deformation and welding between the contacting asperities. It occurs most readily when surfaces are clean (and especially in vacuum) and there are chemical and structural similarities between the materials ("like-on-like" situations being notoriously poor). Archard [4] constructed a simple model in which the true area of contact, which is inversely proportional to the hardness or flow stress of the material, is related to the wear rate by a constant K which is determined by the probability, at each encounter, that a particle of debris is detached. This leads to the expression

$$V \propto L \frac{x}{H}$$

where V is the volumetric wear, L the load, x the sliding distance and H the microhardness. The strain-hardening properties of the material must obviously be considered, alloys such as Hadfield high manganese steel being extremely wear resistant because of a rapid work-hardening process. Kuhlmann-Wilsdorf [5] has stressed the importance of understanding the subsurface dislocation structures that are induced at high rates of strain.

Adhesive wear can be lessened (i) by increasing the hardness H or work hardenability of the metal, (ii) by introducing a suitable (wear-resistant) coating which reduces the tendency of surfaces to weld (its effectiveness can be judged by the coefficient of friction achieved) and (iii) by providing a very smooth and well-conforming surface so that the load is carried more elastically, with less plastic deformation at asperities (lubrication obviously assists in this respect).

Abrasive wear occurs when a hard protuberance or particle of debris indents and cuts a groove in the softer material. The volume of material abraded is proportional to the depth of penetration; it is therefore

again inversely proportional to hardness H and directly proportional to load. Experimental data (Fig. 1) compiled by Moore [6] shows that this is reasonably true up to the point at which the hardness H of the material matches or exceeds the hardness H_a of the abrasive. Then a dramatic reduction in abrasive wear rate occurs, simply because the abrasive particles are no longer able to indent the surface. This fall-off in wear rate as a function of H may reach three orders of magnitude and is especially pronounced for fine abrasives (less than $10 \mu\text{m}$ in size) such as are encountered in industrial applications.

Thus dramatic reductions in abrasive wear rates can be achieved (i) by increasing the microhardness of the surface to a value that exceeds that of the abrasive or of work-hardened or oxidized metallic debris, (ii) by smoothing the surface so that the angle of attack (the cutting angle) of abrasive particles

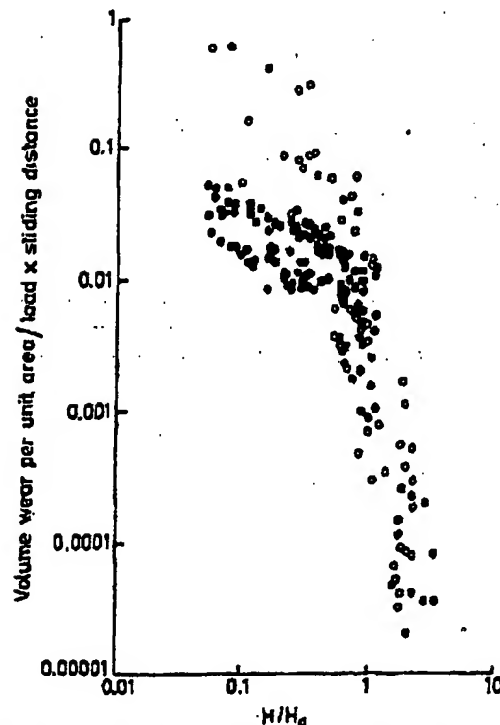


Fig. 1. The volumetric wear rate, measured experimentally for a variety of materials exposed to abrasive wear, as a function of the ratio of the hardness H of the material to the hardness H_a of the abrasive. (After ref. 6.)

is reduced and (iii) by providing a lubrication system which carries debris away from the material surface and so lessens secondary abrasive wear.

Corrosive wear occurs generally when a corrosion product is formed on the metal and is subsequently removed by mechanical action. Spalling of the corrosion film may occur simply as a result of mechanical growth stresses within the scale. An important category of corrosive wear is that termed either oxidative or oxidation wear, which occurs when sliding metal surfaces are oxidized in the atmosphere by frictional heating of asperities. The development of oxide films on steels worn in air can strongly influence their wear rate, as was demonstrated by Welsh [7] and by Hirst and Lancaster [8]. Depending on the sliding speed the wear rate as a function of increasing load undergoes a sharp transition, increasing by about two orders of magnitude. This marks the point at which oxidation and subsurface strain hardening cease to maintain a mild oxidative wear regime and the oxide cracks and spalls off. Welsh [7] showed that there is an optimum substrate hardness condition in order to support the stressed oxide; in a plain carbon steel this Vickers hardness lay between 840 and 425 HV, more or less independent of load. Welsh further observed that incremental loading (i.e. in stages) would allow the mild wear regime to be extended considerably, to higher loads. Some surface change occurs at low loads which tends to inhibit severe wear at higher loads and, by etching the oxide and showing that there was an immediate reversion to severe wear, Welsh showed that it is principally a consequence of oxidation.

Quinn [9] has attempted to develop a detailed model of oxidative wear in which oxidation at asperities heated frictionally proceeds until a critical thickness is reached, at which point the oxide spalls off. This thickness, typically about 3 μm , he determined by microscopy examination of the worn surface. Quinn assumed parabolic oxidation kinetics, i.e. controlled by diffusion of ions through a thickening film; there is very poor agreement, however, with the rate constants for oxidation observed in static tests, the discrepancy being several orders of magnitude. The reason for this is probably that under mechanical stresses the oxide is fractured and so the cor-

rodant has free access to the metal. Dearnaley [10] introduced linear growth rate of the oxide, arriving at the wear formula

$$V = \frac{K_0 t L x}{\delta_c \rho H}$$

in which K_0 is the linear oxidation rate (the mass of oxide per unit time), t is the time of contact for a single junction encounter, L is the load, x is the sliding distance, δ_c is the critical oxide thickness before spalling, ρ is the oxide density and H is the oxide microhardness. Krause [11] has shown that sliding between metallic contacts can cause the oxidation rate to be two orders of magnitude greater than in the case where there is no slip. It is important to recognize that an oxide which may be hard and protective against adhesive and abrasive wear may not be protective against oxidation.

According to this formula, oxidative wear can be reduced (i) by reducing the oxidation rate of the metal by appropriate additions, (ii) by increasing the critical oxide thickness by reducing internal oxide growth stresses and raising the fracture toughness of the oxide, (iii) by increasing the microhardness of the oxide and (iv) by coating the metal with a hard inert substance which neither oxidizes nor spalls.

These considerations show that in each category of wear the microhardness of the surface is strongly correlated with wear rate, and therefore measurement of this parameter can be a useful indication of wear resistance. Dearnaley *et al.* [12] have therefore applied low load Knoop indentation hardness testing to the study of nitrogen-ion-implanted steels and cemented carbides. Apart from microhardness, the work hardenability and the creep resistance of a metal are undoubtedly important factors in determining wear resistance and they must be optimized as well.

8. OBSERVATIONS ON ION-IMPLANTED METALS

Most of the studies of wear resistance in ion-implanted metals have been made following the implantation of nitrogen ions to doses of 10^{17} - 10^{18} ions cm^{-2} at energies of 50-100 keV [13]. In steels it is generally believed that the increases in microhardness [14] and wear

resistance are due to the classic mechanisms of solid solution hardening (by interstitial nitrogen) and dispersion strengthening (by a fine dispersion of hard nitrides such as ϵ iron carbonitride or chromium nitride). These serve to pin dislocations and can be expected to alter the strain-hardening behaviour of the surface layer. It is significant that for hardened AISI 52100 bearing steel, which is highly martensitic, nitrogen ion implantation achieves no increase in either microhardness or wear resistance [14]. Most researchers agree with Pethica and coworkers that all the available hardening modes mentioned above are already effective in this alloy.

A remarkable and fortuitous effect known for many years [15] has been the persistence of the improvement in mechanical behaviour well beyond the depth of penetration of nitrogen ions. At first it was believed that the nitrogen is driven forwards during wear [16] and, although careful experiments confirm that there is indeed some redistribution (prob-

ably along dislocation pathways), this alone is insufficient to account for the duration of the effect. It has recently been established [12, 17] that the mechanical effects are maintained after any significant trace of the implanted nitrogen has disappeared. Hale *et al.* [17] used Auger electron spectroscopy in conjunction with Falex wear testing to show that the wear resistance is maintained to a depth of at least $1\text{ }\mu\text{m}$; Dearnaley *et al.* [12] used microhardness measurements combined with vibratory polishing and $^{15}\text{N}(p, \gamma)$ nuclear reaction analysis to show that the microhardness continues to be enhanced to a depth of at least $5\text{ }\mu\text{m}$ (Fig. 2). In each case the detectable nitrogen had disappeared after erosion to a depth of less than $0.5\text{ }\mu\text{m}$. In metal-on-metal sliding wear (the Falex test) there is evidence [16] for the establishment of a protective oxide film of unusual smoothness, but this explanation is unlikely to account for the persistence of a hardening mechanism during vibratory polishing in an

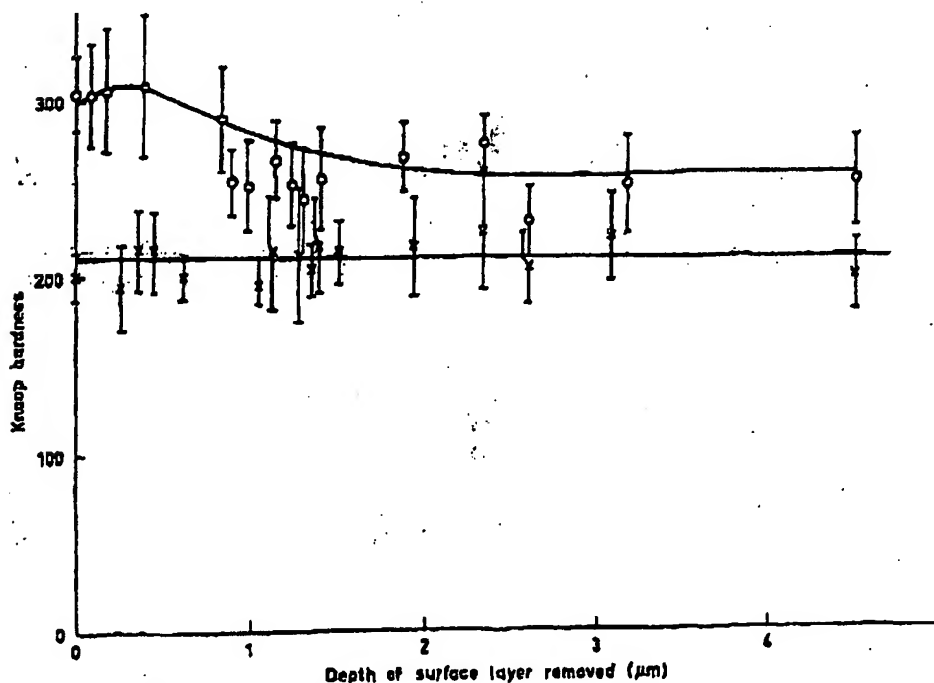


Fig. 2. The Knoop microhardness of a specimen of carbon steel as a function of the thickness of metal removed by vibratory polishing with a slurry of alumina in water: O, nitrogen-implanted area; X, unimplanted area. The load on the indenter was 10 gf. The measured hardness remains greater in the implanted area to a depth of over $4\text{ }\mu\text{m}$, although there is no residual nitrogen detectable after less than $1\text{ }\mu\text{m}$ has been worn away. (From ref. 12.)

alumina-water slurry [12]. Dearnaley *et al.* propose that the nitrogen modifies the strain-hardening processes in the superficial layer and that, once run-in has been completed, this effect may become self-propagating. Presumably this can be tested by observation, using transmission electron microscopy, of the dislocation structure in the implanted and unimplanted regions. Hubler and Smidt [18] present a somewhat similar argument based on elasto-plastic modification of surface asperities ("shake-down"), leading to an enhancement of run-in mechanisms.

Some pronounced increases in microhardness and wear resistance as a result of nitrogen ion implantation into alloys such as Ti-6Al-4V (where the composition is given in approximate weight per cent) [19] are most probably due to the dispersion of titanium oxynitride precipitates that has been observed by transmission electron microscopy. The work by Hutchings and Oliver [19] shows conclusively that there is no persistence of the improvement in wear rate, once the nitrogen-containing layer has been worn away.

The other light interstitial species, carbon and boron, give similar increases in wear resistance when implanted into steels but there has been less exploration of the detailed properties since intense ion beams of these elements are less easily generated.

Much greater attention has been given to the effects of implanting a number of metallic species into steel; these include Ti^+ , Ta^+ , Mo^+ , Sn^+ and Y^+ ions. Thus high dose implantations of titanium have produced low friction wear-resistant surfaces [20, 21] although low dose Ti^+ ion implantations have been reported to give anomalously high friction coefficients and to exhibit considerable surface wear [22] and enhanced adhesion. There is clear evidence [23] that Ti^+ ion implantation alone is less effective than a treatment in which titanium and carbon are introduced together, either by a dual implantation or by surface carbonization followed by inward diffusion. Follstaedt *et al.* [23] attribute the low friction condition to the formation of an amorphous Fe-Ti-C film. The other strong carbide-forming elements tantalum, niobium and vanadium probably behave in a similar fashion.

It is not clear whether tin introduced by ion implantation or ion beam mixing [24]

acts in iron by the formation of hard inter-metallic compounds (the presence of which is revealed by Mössbauer spectrometry) or by a modification of surface oxide growth, leading to the incorporation of SnO_2 into the film generated during mild oxidative wear. Further work, by Hale and others, is in progress on this topic. Tin implantation seems effective at doses as low as 10^{16} ions cm^{-2} , and this tends to suggest an oxidative rather than a mechanical explanation.

Yttrium implanted into chromium-containing steels (such as type 304 stainless steel) even at very low concentrations of around 0.1 at.% will reduce wear. No benefit, and possibly a degradation, is observed in pure iron, however. An even better result in stainless steel is achieved if the yttrium implantation is combined with a (normal dose) ion implantation of nitrogen. These observations are consistent with the known influence of yttrium in the formation of a fine-grained adherent Cr_2O_3 film during thermal oxidation of alloy steels. Yttrium ion implantation, however [25], has been shown to improve dramatically the wear resistance of a tool steel containing only 0.5 at.% Cr and to stimulate the induction of a low friction wear mode. It is also known to benefit the wear in plain carbon steel (En8).

A comparison of the microhardness changes and the wear resistance of several steels ion implanted with Ti^+ , Ta^+ , Sn^+ , Y^+ and Pt^+ ions is now being made by Waddell and Dearnaley [25] in order to establish the chemical and physical role of these additives better. It is possible that the interaction between oversized atoms, such as yttrium or platinum, and interstitial nitrogen due to the elastic strain field surrounding the substitutional species leads to the formation of substitutional-interstitial pairs. The resulting pairs or dipoles can interact strongly with dislocations over a much wider temperature range than can interstitial atoms acting alone. Baird and Jamieson [26] call this "interaction solid solution strengthening", and Cuddy *et al.* [27] have shown that the hardening effects in Fe-Ti-C alloys containing 2 at.% Ti are due to this rather than to dispersion hardening by second-phase TiC particles or solid solution hardening due to titanium alone. Ion implantation allows this model to be tested effectively,

especially with chemically inert atoms such as platinum.

4. ION BEAM MIXING AND ION-BEAM-ENHANCED DEPOSITION

The versatility of the ion implantation process for the protection of metals has been further extended over recent years by the development of two additional hard vacuum processes which can be carried out by a straightforward adaption of the implantation equipment. In terms of the incident ion energies, the ion source technology, the absence of throwing power and thus the need for workpiece manipulation, these techniques lie much closer to the field of ion implantation than they do to ion plating or other plasma-assisted processes.

Ion beam mixing occurs when a thin deposited coating is bombarded with ions which can penetrate the interfacial region and stimulate intermixing by a combination of (rapid) collisional processes in the collisional cascade and (much slower) diffusional mechanisms, such as radiation-enhanced diffusion [24]. A recent development in understanding has come from the recognition [26] that thermodynamic driving forces such as the heat of formation of compounds can be effective even during the brief period of collisions within the cascade. This is less surprising when we recall that recombination of interstitials and vacancies can certainly occur during this stage, and the chemical interactions simply combine with elastic interaction potentials. Ion beam mixing can be used to render a surface film more adherent (this is sometimes referred to as ion beam "stitching") or to bring about a complete intermixing, even resulting sometimes in the formation of a buried layer, by the action of the inverse Kirkendall process [24].

Ion-beam-enhanced deposition is the term given to the bombardment of coating films by relatively low energy ions (designed to stop within the coating) to modify its structure and composition. The process takes place by increasing the lateral mobility of the deposited atoms so that a more dense structure is achieved; such coatings can be very smooth. The bombardment can be carried out continuously or as a cyclic process of alternate deposition and ion bombardment [29].

Both ion beam mixing and ion-beam-enhanced deposition can usefully be performed with reactive ions, e.g. of nitrogen. The penetration of these lighter ions is advantageous in reaching the interface without requiring very high energies. Strongly bound nitrides can be produced, and it is as a result of these that the surface can be rendered hard, chemically inert and with interesting optical properties. Thus Kant *et al.* [29] have formed a coating approximately 200 nm thick consisting of titanium carbonitride ($\text{TiC}_{0.3}\text{N}_{0.8}$) on a substrate of (hard) AISI 52100 bearing steel. This layer was produced by the implantation of copious doses of nitrogen ions at 30 keV energy into titanium, put down in sequentially deposited layers of about 1 nm thickness. The coating proved to be highly adherent and wear resistant, with the added advantage of a low coefficient of friction against steel (0.2).

The practical difficulty of the ion-beam-enhanced deposition process lies in the fact that intense doses of nitrogen or other beams are required, in excess of 10^{18} ions cm^{-2} . However, ion source technology is being developed rapidly to meet the needs of the silicon device industry, for buried isolation, and currents of 100 mA or more of gaseous ions are now available from a variety of ion sources.

5. DISCUSSION

In the light of these observations we can now consider ways in which the present techniques of ion implantation, together with the associated procedures for ion beam mixing and ion-beam-enhanced deposition, can best be used in order to protect metals against various forms of wear.

We have seen that it is difficult to reduce substantially the rate of adhesive wear, since it depends only on the inverse power of microhardness. It is far better to bring about a speedy transition to abrasive wear conditions and at the same time to ensure that the microhardness of the material surface exceeds that of any abrasive particles present (including work-hardened or oxidized debris). For a titanium alloy this principle has been well demonstrated [2] in quantitative wear tests using thin layer activation to study erosion and transfer of titanium wearing against high

molecular weight polyethylene (for hip joint replacement). The investigation showed that debris from the metal is quickly embedded in the surface of the polymer. This debris is almost certainly in the form of TiO_2 , which is harder than the alloy and continues to abrade it. Ion implantation of high doses of nitrogen (greater than 10^{27} ions cm^{-2}) raises the surface microhardness considerably (by dispersion strengthening with titanium oxynitride) to a value well above that of TiO_2 . In accordance with our understanding of abrasive wear the wear rate was reduced by a factor of between 500 and 1000. This compensates considerably for the shallowness of the implanted layer and the possible absence of a persistent strain-hardening mechanism in this alloy.

It follows from this that the best protection will be achieved by implantations or other treatments designed to produce a high surface hardness. The attempts by Guzman *et al.* [30] to form boron nitride by reactive ion beam mixing of a deposited boron film are notable in this respect, while Satou *et al.* [31] claim to have produced films containing a proportion of extremely hard cubic BN by the ion-beam-enhanced deposition process. Boron ion beams, if they can be made available with the necessary intensity, can also be used to advantage for implantation or reactive ion beam mixing, because a number of metal borides have very high hardness values.

It is not sufficient, however, to create a very hard surface film since, as Welsh showed [7], it requires to be mechanically supported if it is not to crack and to spall off under load. Moreover the internal stresses and stress gradients within the film must be controlled. It follows that the first step in protecting a metal from wear must be a through-hardening process to enhance the bulk properties of the alloy. The next step is to optimize near-surface hardness still further, e.g. by nitriding or carburizing. After it has been finish machined, this surface is suitable for ion implantation, using nitrogen (or boron) ions at relatively high energies. This series of treatments is just what is now being employed industrially to obtain very long lifetimes for screws used for the injection moulding of filled plastics.

It is advantageous at the ion implantation stage to incorporate minor additions of

species such as yttrium or tin, which have been shown to enhance the performance of implanted nitrogen. The fact that the doses of these elements required are relatively low (less than 10^{18} ions cm^{-2}) means that sputtering does not limit their retention even in components of complex shape. Ideally these species are introduced simultaneously with nitrogen ions, e.g. by use of a sputtering ion source.

A preferred after-treatment would then consist of the deposition of a thin surface coating of a suitable metal, such as titanium or vanadium, and ion beam mixing of this into the substrate. The ion beam mixing can be done reactively, e.g. with nitrogen ions which may assist in converting the coating to nitride. Onto this ion-beam-mixed surface can then be built up any required thickness of ion-beam-enhanced deposition coating, simply by continuing the film deposition and at the same time reducing the ion energy in order to concentrate the bombardment within the overlay coating. Once again the composition can be controlled reactively in such a process in order to obtain a maximum degree of microhardness coupled with a chemical inertness, which contributes to the minimization of adhesion.

The treatment described has several advantages (and disadvantages) by comparison with existing methods of coating materials by chemical vapour deposition or physical vapour deposition. Firstly, the temperature at which it may be carried out is low, probably no more than 250°C for steel, since vacancy-assisted mixing takes place at such a temperature. Distortion of tools would therefore be minimal. The ion beam mixing step can achieve excellent adherence because the interfacial zone can controllably be extended to 10-100 nm. The subsequent ion-beam-enhanced deposition process results in very coherent dense films because the deposited energy rate is high and lateral diffusion of atoms ensures a smooth layer, possibly even filling scratches in the original metal surface. Such dense structureless coatings are obtained in ion plating only at relatively high temperatures. The smoothness of the films [29] aids in lubrication and in the important run-in stage of wear. It also lessens metal pick-up on a metal-forming or cutting tool, a process which is known to be troublesome in surfaces

with nodular coatings. The dimensional changes produced by ion-beam-enhanced deposition are small (about $0.2 \mu\text{m}$) and therefore compatible with many precision components or knife edges; the techniques, being line of sight, can be applied to one face of a knife or punch to achieve a self-sharpening action. The attention which can be given to grading the microhardness and composition of the coating and its substrate controllably is perhaps the best feature of this group of processes. Finally, the whole sequence of steps can be carried out automatically during a single pumpdown of the facility.

6. SUMMARY

Ion implantation of nitrogen into steels and other alloys produces surface hardening and wear resistance, particularly under conditions of abrasive wear. In steels it has been demonstrated that this condition persists even after the implanted nitrogen has been worn away, and it appears that a favourable condition of work hardening is brought about during the initial "running-in" of a nitrogen-implanted steel. There is no such persistence in titanium.

Other elements, such as yttrium or titanium, when implanted into steels can also give surface hardening and wear resistance, but only if accompanied by interstitial species such as nitrogen or carbon. The two possible explanations, in terms of (i) interaction solid solution strengthening by pairs of substitutional and interstitial atoms reorienting in the strain field of nearby dislocations and (ii) dispersion strengthening by second-phase carbide or nitride precipitates, are at present being tested.

Further protection of metals against wear can be achieved by thin hard coatings which can be applied by ion-beam-enhanced deposition. In this way, titanium or boron can be caused to undergo ion beam mixing with the substrate by nitrogen ion bombardment which in the subsequent phase of coating is controlled so as to convert the surface to a hard nitride.

In this way, both adhesive and oxidative modes of wear can be largely suppressed, and the rate of abrasive wear is reduced by ensuring that the surface hardness exceeds that of metallic wear debris or deliberately introduced abrasive fillers.

ACKNOWLEDGMENT

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ION IMPLANTATION. A process for introducing alloying elements into a host material by accelerating the ions to a high energy (at least tens of kilovolts) and allowing them to strike the surface of the host. The impinging atoms penetrate into the substrate material to a depth of 0.01 to 1 micrometer, depending on the atomic number and energy of the atom, and create a thin alloyed surface layer on the substrate. The process differs from others, such as electroplating, in that it does not produce a discrete coating, but rather it alters the chemical composition near the surface of the base material.

In recent years, the electronics industry has made increasing use of ion implantation as a method of doping semiconductors. Since the number of ions implanted is determined by the charge transferred to the substrate and their depth distribution by the incident energy, ion implantation has improved the controllability and reproducibility of certain semiconductor device processing operations. Also, ion implantation processes do not require the high temperatures needed to introduce impurities by diffusion. Thus the limitations arising from the changes produced in materials by high temperature are eased. Ion implantation also has been used in electronics to change the magnetic properties of substrates used for magnetic bubble devices.

Ion implantation also has promise in other fields involving surface technology; for example, new metallurgical phases with prior unknown properties can be formed. In some cases, such as heavy implantations of tantalum in copper or phosphorus in iron, amorphous or glassy phases can be formed. Or, if the implanted atoms are mobile, inclusions and precipitates can be formed as, for example, implanted argon and helium atoms are insoluble in metals and may form bubbles. The composition of a surface layer can be changed by differential sputtering caused by the implanted ions.

The damage and high concentrations of lattice defects, resulting from atomic displacements produced by the incident atoms, can change the chemical reactivity and mechanical hardness of a treated surface. Implantation can enhance the diffusion of impurities already deposited in a substrate, presumably through the motion of the high concentrations of lattice defects produced by the incident ions.

One of the most promising nonelectronic applications of ion implantation involves surface treatment to improve the hardness and wear resistance, as well as lowered susceptibility to corrosion, of metals. In some experiments, the benefits of ion implantation on wear may persist to a depth 10^3 times that of the implanted layer thickness. The implanted atoms are apparently transported into the metal as a tool wears. Thus, the technology is of large interest in connection with improving cutting tools and bearings. Some experiments have suggested that nitrogen implantation increases the fatigue life of carbon steel parts. The results are consistent with present understanding of the mechanisms of fatigue failure. It is well known that fatigue cracks start at the surface and that there is a close connection between surface hardness and fatigue life. Compressive stresses due to the presence of additional implanted ions may also play a role in the suppression of crack initiation.

The production of corrosion-resistant materials by alloying is well established, but the mechanisms are not fully understood. It is known, of course, that elements like chromium, nickel, titanium, and aluminum depend for their corrosion resistance upon a tenacious surface oxide layer (passive film). Alloying elements added for the purpose of passivation must be in solid solution. The potential of ion implantation is promising because restrictions deriving from equilibrium phase diagrams frequently do not apply (i.e., concentrations of elements beyond the limits of equilibrium solid solubility might be incorporated). This can lead to heretofore unknown alloyed surfaces which are very corrosion resistant.

Ion plating is another area of surface treatment. Ion plating is carried out in a gaseous electrical discharge in which the substrate to be plated is the cathode. The discharge is created by an applied potential of 500 to 5000 V. The primary component of the gaseous environment usually is an inert gas, most often argon. Atoms of the material to be plated are introduced into the gas by evaporation from a heated source. A fraction of the atoms injected by evaporation are ionized before striking the substrate. In ion plating, atoms arrive at the surface with energies of only a few hundred volts and penetrate no more than a few lattice constants into the substrate. Thus, ion implantation produces an alloyed surface layer whose composition varies continuously with depth because of the rather broad distribution of the ranges of the im-

planted ions, while ion plating produces a coating, the composition of which is independent of the nature of the substrate.

Semiconductor Applications. In semiconductor manufacture, area of the workpiece into which ions are implanted is quite small. Homogeneity is sought in semiconductor applications, that is, the concentration of the implanted species should not vary by more than a few percent over the surface of a wafer. The implantation of ions into semiconductors is usually patterned, that is, some areas of the substrate are covered by a mask that stops the incident ions before they enter the substrate. A doped layer in which the implanted atoms are locally in equilibrium phase is usually desired. Thus, implantation is usually followed by a high-temperature annealing treatment, which removes radiation damage through diffusion of lattice defects to defect sinks and recrystallization of disturbed regions. Laser annealing has been used successfully. Laser annealing affects only a surface layer approximately equal to the depth of typical implantations, leaving the bulk of the piece unaltered.

See also **Semiconductors**.

IONIZATION. A process which results in the formation of ion pairs. Such processes occur in water, liquid ammonia, and certain other solvents when polar compounds (such as acids, bases, or salts) are dissolved in them. Dissociation of the compounds occurs, with the formation of positively- and negatively-charged ions, the charges on the individual ions being due to the gain or loss of one or more electrons from the outermost orbits of one or more of their atoms. The ionization of gases is a process by which atoms in gases similarly gain or lose electrons, usually through the agency of an electrical discharge, or passage of radiation, through the gas.

Ionization by collision is an ionization process occurring by removal of an electron or electrons from an atom as the result of the energy gained in a collision with a particle (or quantum of radiation) possessing sufficient energy.

Specific ionization is the number of ion pairs formed per unit distance along the track of an ion passing through matter. This is sometimes called the total specific ionization to distinguish it from the primary specific ionization, which is the number of ion clusters produced per unit track length. The relative specific ionization is the specific ionization for a particle of a given medium relative either to that for (1) the same particle and energy in a standard medium, such as air at 15°C and 1 atmosphere, or (2) the same particle and medium at a specific energy, such as the energy for which the specific ionization is a maximum.

Total ionization is a term used to denote either the total specific ionization (defined above); or the total electric charge on the ions of one sign when the energetic particle that has produced these ions has lost all of its kinetic energy. For a given gas the total ionization is closely proportional to the initial energy and is nearly independent of the nature of the ionizing particle. It is frequently used as a measure of particle energy.

Minimum ionization is the smallest possible value of the specific ionization that a charged particle can produce in passing through a particular substance. When the specific ionization produced along the path of a charged particle is plotted as a function of the particle energy, minimum ionization appears as a broad dip, bound on one side by a rather sharp rise for decreasing particle energy, and on the other side by a gradual rise for increasing particle energy. For singly charged particles in ordinary air, the minimum ionization is about 50 ion pairs per centimeter of path. In general, it is proportional to the density of the medium and the square of the charge of the particle. It occurs for particles having velocities of 95% of the velocity of light, which corresponds to a kinetic energy of 1 MeV for an electron, 2 BeV for a proton and 8 BeV for an alpha-particle.

Ionization potential is the energy per unit charge, for a particular kind of atom, necessary to remove an electron from the atom to infinite distance. The ionization potential is usually expressed in volts, and is numerically equal to the work done in removing the electron from the atom, expressed in electron-volts. See also **Chemical Elements**.

IONIZATION CHAMBER. An instrument constructed to measure the number of ions within a gas-filled enclosure between two elec-

gears are those imaginary circles that are equivalent to the peripheries of a pair of friction wheels that would operate without slipping at the same velocity ratio and center distance as the gears themselves. The point of tangency *P* of the pitch circles on the line of centers is the pitch point of the gearing. The smaller of the two gears is usually referred to as the pinion.

SPURIOUS CORRELATION. Correlation that is misleading. Take two variables *x* and *y* which are independent. Consider a third variable *z* which is correlated with *x* and with *y*. Form $v = f(x, z)$ and $w = f(z, y)$, then frequently *v* and *w* will show considerable dependence which may be traced to the correlation of *x* with *z* and *y* with *z*. In general, then, spurious correlations may be defined as correlation which is introduced by other variables rather than the ones under study.

The real question at issue in correlation is actually this: Are the variables in which we are interested *x* and *y* or *v* and *w*? If the variables are *x* and *y* then the correlation of *y* with *w* is spurious. If the casual variables, however, are *v* and *w* and not *x* and *y*, then the correlation of *v* and *w* is valid and not spurious. The term "spurious" is perhaps itself misleading. It does not imply that the correlation does not exist; only that it may be due to a rather circuitous train of casual influences.

Sir Maurice Kendall, International Statistical Institute, London.

SPURIOUS RADIATION. Any radiation from a transmitter other than that produced by the carrier and its normal sidebands. A radiated harmonic of the carrier is one example of a spurious radiation.

SPUTNIK. The first artificial satellite, one of a series of Russian earth-orbiting satellites, launched on October 4, 1957.

SPUTTERING. 1. In a gas discharge, material is removed, as though by evaporation, from the electrodes, even though they remain cold. This phenomenon is known as sputtering. 2. The term is also used for the corresponding phenomenon when the discharge is through a liquid. In the first case, sputtering is a nuisance that limits the life of a device; in the second case, it is put to work to make colloidal solutions of metals. 3. A result of the disintegration of the metal cathode in a vacuum tube due to bombardment by positive ions. Atoms of the metal are ejected in various directions, leaving the cathode surface in an abraded and roughened condition. The ejected atoms alight upon and cling firmly to the tube walls and other adjacent surfaces, forming a blackish or lustrous metallic film. This effect is often utilized to form very fine-grained coatings of metal upon surfaces of glass, quartz, etc., purposely exposed to the sputtering. Films of different metals can be obtained by using cathodes made of these metals. Glass plates may be thus silvered, or suspension fibers of spun quartz rendered conducting for use in electrometers, etc.

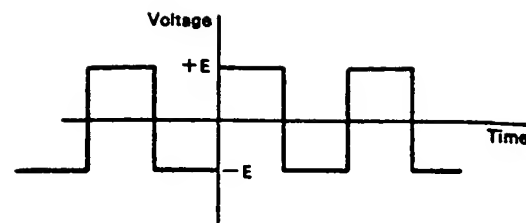
SQUALL. See *Fronts and Storms*.

SQUARE AND SQUARE ROOT. The square of a number or quantity is the product of that number or quantity when multiplied by itself. Hence, 4×4 yields 16, the latter being the square of 4. Similarly, the number 4 is termed the square root of the number 16. The process of raising any number to any integral power, as in squaring (a power of 2) or in cubing (a power of 3) is known as *involution*. The process of extracting roots, that is, of finding that 4 is the square root of 16, or of finding that 3 is the cube root of 27, is known as *evolution*. See also *Exponent*; *Number Theory*; *Radical (Mathematics)*; and *Root (Mathematics)*.

SQUARE LAW MODULATOR. A device whose output is proportional to the square of its input. The carrier and modulating signal are added in the input to produce a modulated carrier in the output.

SQUARE WAVE. A square wave, as the name indicates, has the wave form shown in the figure.

Any periodic wave, regardless of its shape, may be analyzed into a series of sine and cosine components whose frequencies are harmoni-



Square wave.

cally related. The number of these components will be determined by the shape of the wave, but in general the sharper the corners of the original wave the more component terms. Thus a square wave will require a wide range of frequencies to express it. These components are not mere mathematical fictions but are true electrical components in the case of an electric wave. They may be separated and examined by means of proper filter circuits. Since a square wave will contain a long series of frequencies it may be used for rapidly determining the frequency response of a piece of equipment by applying the wave to the input and noting the distortion of the output wave. The distortion is due to certain frequencies of the original wave being attenuated or amplified out of proportion in passing through the circuit. Thus the necessity of making a laborious series of tests at various frequencies using sine waves is avoided. When an operator is properly trained in interpreting the results of such testing it offers a rapid means of checking amplifiers, networks, etc. These square waves may be generated by a variety of electronic circuits.

SQUASH. Of the family *Cucurbitaceae* (gourd family), squash plants are of three major species and one minor species of the genus *Cucurbita*. These several species, plus the designations of summer and winter squash, tend to complicate a classification of these plants. There is not a direct relationship between species or growth pattern and whether a plant is a summer or a winter variety. Although a majority of squash plants assume an indeterminate growth pattern as vinelike, tendril-bearing herbs, some take the more determinate form of bushes or semibushes. In terms of food value, the winter squash is rated very high among all vegetables. Winter squash usually is baked or used in pies. Varieties of winter squash more closely resemble the pumpkin, and canning and freezing processes are very similar. Many, but not all varieties of winter squashes are members of the species *Cucurbita maxima*. Some also are members of *C. moschata* and *C. mixta*. Varieties of *C. maxima* and *C. moschata* can be crossed artificially, but such crossing does not occur naturally in the field.

Specific Varieties. The genus *Cucurbita* is indigenous to the Americas. The largest concentration of wild species is in Mexico, in a vast area from just south of Mexico to the border between Mexico and Guatemala. The cultivated species *C. pepo*, *C. mixta*, and *C. moschata* are North American, whereas *C. maxima* is from South America. Because of the uncharted movement of pre-Columbian peoples and their crops in the Americas, it is difficult to pinpoint the exact area of origin of the cultivated species. One authority suggests that *C. pepo* is native to the southwestern United States and northern Mexico. *C. moschata* and *C. mixta* are lowland species ranging from Vera Cruz, Mexico, southward through Central America. In this area, cultivars of *C. mixta* are much used for their tasty, edible seeds.

Through years of cultivation, research, and experimentation, numerous varieties of squash have been developed. See accompanying illustration.

Pollination. Squash plants have unisexual flowers. In order to produce fruit, squashes require cross-pollination—that is, the transfer of pollen from the anthers of the male flower to the stigma of the female flower. Inadequate pollination results in reduced yield and misshapen fruit. Bees provide the primary means of pollen transfer, and often bee hives are used. Experienced growers will have one hive for every 3 to 4 acres (1.2 to 2 hectares) of squash plants. Beehives are placed in the center of the field so that bees do not have to travel more than a few hundred feet to feed. Obviously, there should be no insecticide applications during the flowering period.